

Controlling ultracold chemical reactions via Rydberg-dressed interactions

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We show that ultracold chemical reactions can be manipulated and controlled by using Rydberg-dressed interactions. Scattering in the ultracold regime is sensitive to long-range interactions, especially when weakly bound (or quasi-bound) states exist near the collision threshold. We investigate how, by Rydberg-dressing a reactant, one enhances its polarizability and modifies the long-range van der Waals collision complex, which can alter chemical reaction rates by shifting the position of near threshold bound states. We carry out a full quantum mechanical scattering calculation for the benchmark system H_2+D , and show that resonances can be moved substantially and that rate coefficients at cold and ultracold temperatures can be increased by several orders of magnitude.

A key advantage of ultracold systems is the extraordinary degree of control they provide, such as tunable interactions through Feshbach resonances [1] used to investigate degenerate quantum gases [2–4]. This control allows to probe exotic three-body Efimov states [5], and to study ultracold molecules [6, 7] and modify their chemistry [8–10], *e.g.*, by orienting them [6, 11]. Another approach to modify interactions is to excite atoms into Rydberg states [12], where they acquire extreme properties (*e.g.*, long lifetimes or large electric dipole moment) [13]; long-range Rydberg *trilobite* molecules [14, 15] or *macrodimers* [16, 17] exemplify these exaggerated properties. The control over strong interactions led to proposals for quantum computing [18], *e.g.*, to achieve quantum gates [19, 20] or study quantum random walks [21], and to the excitation blockade mechanism [22], where a Rydberg atom prevents the excitation of nearby atoms [12, 23–26]; this effect is used to realize electromagnetically induced transparency [27, 28], to generate single photons [29] and photon-photon interactions [30, 31], or non-destructive imaging of Rydberg atoms [32] to study dynamics of energy transport [33].

Recent studies propose using Rydberg dressing to explore many-body physics [34, 35] such as dipolar BEC [36], supersolid vortex crystals in BEC [37] and to cool polar molecules [38]. In this letter, we show how ultracold chemical reactions can be modified and controlled by Rydberg-dressing an atom approaching a diatom, which increases its polarizability and modifies the atom-diatom van der Waals complex and the reaction rate. We consider H_2+D , a benchmark system for quantum calculations explored extensively at ultralow [39] and higher temperatures [40], and for which accurate *ab initio* potential energy surfaces (PES) [41, 42] exist. Here, the deuterium atom D is Rydberg-dressed by weakly coupling its ground state $|g\rangle$ to a Rydberg state $|r\rangle$ of width γ_r using a far detuned continuous-wave (CW) linearly polarized laser (see Fig. 1(a)). At large separation, when the atom-molecule interaction is negligible, the atom can be modeled as a two-level system. The CW laser, described by an oscillating electric field $\mathcal{E} \cos \omega_L t$

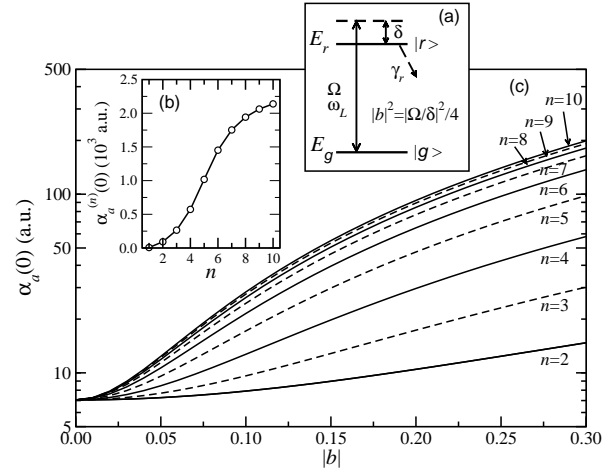


FIG. 1: (a) Sketch: the ground state $|g\rangle$ of energy E_g is dressed by a laser of frequency ω_L blue-detuned by δ from a Rydberg level $|r\rangle$ of energy E_r and natural width γ_r (Ω and $|b|^2$ are the Rabi frequency and fraction of Rydberg state, respectively). (b) Static polarizability of D excited into a state np for $n \leq 10$. (c) Static polarizability of D as a function of the Rydberg-dressing coefficient $|b|$ (see text for details).

of strength \mathcal{E} and frequency ω_L , couples $|g\rangle$ (energy E_g) and $|r\rangle$ (energy E_r) with Rabi frequency $\hbar\Omega = \langle g|\mu\mathcal{E}|r\rangle$, (μ : dipole transition moment). The detuning δ is defined by $\hbar\delta = \hbar\omega_L - (E_r - E_g)$.

Under far-detuning ($|\delta| \gg \gamma_r$) and low laser power ($|\Omega| \ll |\delta|$) conditions, the state of the atom (up to a global phase) within the rotating wave approximation (RWA) is $|a\rangle \approx \sqrt{1 - |b|^2}|g\rangle + b|r\rangle$, where $b = \frac{1}{2}(\Omega/\delta)e^{-i(\omega_L t - \phi_0)}$, and ϕ_0 is an initial phase. Properties of dressed atom can be obtained using $|a\rangle$; *e.g.*, its dynamic polarizability $\alpha_a(\omega)$ and dipole moment d_a

$$\alpha_a(\omega) = (1 - |b|^2) \alpha_a^{(g)}(\omega) + |b|^2 \alpha_a^{(r)}(\omega), \quad (1)$$

$$d_a = (1 - |b|^2) d_a^{(g)} + |b|^2 d_a^{(r)}, \quad (2)$$

where $\alpha_a^{(j)}(\omega) = \sum_{k \neq j} \frac{2\omega_{jk} |\langle j|\mu|k\rangle|^2}{\hbar(\omega_{jk}^2 - \omega^2)}$ and $d_a^{(j)} = \langle j|\mu|j\rangle$ are

the dynamic polarizability and dipole moment of the atom in state $|j\rangle$, respectively: $\hbar\omega_{jk} \equiv E_k - E_j$, and the fast oscillating cross terms containing $\langle g|\mu|r\rangle$ are neglected. The static polarizability $\alpha_a^{(r)}(0)$ for Rydberg states is usually much larger than that of the ground state $\alpha_a^{(g)}(0)$ (since $\hbar\omega_{jk}$ can be small). A linearly polarized laser can excite D (or an alkali atom) from its atomic s ground state into a Rydberg state $|j\rangle = |n, \ell_e, m_\ell\rangle$ (with principle quantum number n , electron angular momentum $\ell_e = 1$ with projection $m_\ell = 0$); Fig. 1(b) shows the rapid growth of $\alpha_a^{(n)}(0)$ for the np state of D ($n \leq 10$). Note that without external fields mixing states of different parities, $d_a^{(j)} = 0$ (e.g., for D in a pure np state). While $d_a^{(g)}$ remains small, even a weak electric field leads to Stark splittings of Rydberg states: in the linear Stark regime, the highest state of a given manifold n has a large dipole moment $d_a^{(n)} = \frac{3}{2}n(n-1)$ a.u. [34]. Even with a small mixing $|b|^2 = |\Omega/\delta|^2/4$, a Rydberg-dressed atom can still possess a large polarizability (see Fig. 1(c)) and in some cases a large dipole moment which determine the long-range interaction with another atom or molecule.

In Fig. 2(a), we sketch the PES's dependence on the reaction coordinates (*i.e.* the distance between H_2 and D in the entrance channel, and HD and H in the exit channels). Rydberg-dressing D changes the long-range interaction in the entrance channel; for H_2 in its ground electronic state (no permanent dipole moment), the leading interaction $-C_6/R^6$ depends on the van der Waals coefficient C_6 . Here, we assume the distance R between D and H_2 is large enough, and neglect the anisotropy of H_2 . Note that if the molecule has a permanent dipole moment (e.g., for heteronuclear molecules) and the atom is Rydberg dressed to a Stark state, the leading interaction is the dipole-dipole interaction. Two components contribute to $C_6 = C_6^{(ind)} + C_6^{(dis)}$, a dipole induced-dipole term $C_6^{(ind)} \propto d_a^2$, and a dispersion term $C_6^{(dis)} \propto \alpha_a$. By changing α_a and d_a using Rydberg-dressing, one can modify the long-range atom-molecule van der Waals complex, and affect scattering properties.

The dispersion term $C_6^{(j,dis)}$ for an atom in state $|j\rangle$ can be evaluated by the Casimir-Polder integral

$$C_6^{(j,dis)} = \frac{3}{\pi} \int_0^\infty \alpha_m(i\omega) \alpha_a^{(j)}(i\omega) d\omega, \quad (3)$$

where α_m and $\alpha_a^{(j)}$ are the dynamical polarizability of the molecule and of the atom, respectively. Inserting Eq.(1) into the Casimir-Polder integral gives

$$C_6^{(dis)} = C_6^{(g,dis)} + |b|^2 \Delta C_6^{(r,dis)}, \quad (4)$$

where $\Delta C_6^{(r,dis)} \equiv C_6^{(r,dis)} - C_6^{(g,dis)}$. The corresponding induction term is $C_6^{(j,ind)} = \frac{2}{3}[d_a^{(j)}]^2 (\alpha_{zz} - 2\alpha_{xx})$ [43], where α_{pq} is the pq component of the cartesian static molecular dipole polarizability tensor (with z along the

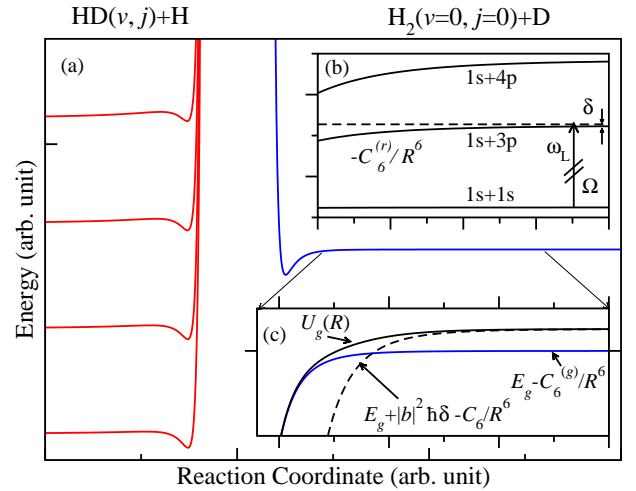


FIG. 2: (Color online) (a) Sketch of the PES vs. reaction coordinates (see text) showing exit channels (left curves) nearest to the entrance channel on the right. (b) Rydberg dressing by a blue-detuned laser ($\delta > 0$) to avoid crossing a Rydberg curve. (c) Long-range interaction in the entrance channel: the dressed curve $U_g(R)$ (solid black line) is more attractive with its threshold lifted from the bare case (blue solid line). $U_g(R)$ transitions smoothly from its asymptotic form (dashed line) at large separation to the bare curve at shorter range.

TABLE I: Calculated C_6 terms for a Rydberg-dressed D atom interacting with a ground state H_2 molecule: $[n]$ denotes 10^n .

n	$C_6^{(n,dis)}$ (a.u.)	$C_6^{(n,ind)}$ (a.u.)	n	$C_6^{(n,dis)}$ (a.u.)	$C_6^{(n,ind)}$ (a.u.)
1	7.053	0.000	5	1.018 [3]	1.030 [4]
2	9.241 [1]	1.030 [2]	6	1.452 [3]	2.317 [4]
3	2.640 [2]	9.266 [2]	7	1.751 [3]	4.540 [4]
4	5.720 [2]	3.706 [3]	8	1.942 [3]	8.072 [4]

molecular symmetry-axis). Inserting Eq. (2) and noting that $d_a^{(g)} = 0$, we find $C_6^{(ind)} = |b|^4 C_6^{(r,ind)}$.

The components of C_6 for the benchmark system H_2+D , tabulated in Table I, show a rapid increase with n . They were computed using the TD-DFT/vdW method [43] developed to obtain the dynamic polarizability for H_2 using the large aug-cc-pVTZ basis set [44] and the PBE0 density function. The dynamic polarizability of D was computed using Gauss-Laguerre quadrature, where the integration grid and number of excited states (computed using the proper reduced mass for D) was converged to provide an accuracy better than 0.1% (continuum contributions were omitted for D, suggesting a 5-10% underestimate of $C_6^{(n,dis)}$). C_6 was computed using gaussian quadrature, with the induced term calculated for the highest Stark-splitted state for a given n .

In our benchmark example H_2+D , we consider dressing D with a CW laser blue-detuned ($\delta > 0$) from $3p$

(Fig. 2(b)) to prevent populating the Rydberg state; as D approaches H_2 , the detuning increases leading to a weaker effect. For simplicity, we also consider no static field and omit $C_6^{(\text{ind})}$; we can then drop the superscript (dis) and write $C_6 = C_6^{(g)} + |b|^2 \Delta C_6^{(r)}$. Within the RWA, the Hamiltonian for the internal degrees of freedom at a fixed large separation R can be written as a 2×2 matrix (in the basis $|am\rangle \equiv |a\rangle \otimes |m\rangle$ where $|a\rangle = |g\rangle$ or $|r\rangle$ is the atomic state, and $|m\rangle$ the state of the molecule):

$$H = \begin{pmatrix} -C_6^{(g)}/R^6 & \hbar\Omega/2 \\ \hbar\Omega^*/2 & -\hbar\delta - C_6^{(r)}/R^6 \end{pmatrix}, \quad (5)$$

where the ground state atom-molecule collision threshold is set to zero. By diagonalizing (5), we obtain two Born-Oppenheimer curves: a dressed ground curve U_g between H_2 and ground-state D (dressed by $|r\rangle$), and a dressed excited curve U_r between H_2 and excited D (dressed by $|g\rangle$). Assuming $|\Omega/\delta| \ll 1$ and $C_6^{(r)} > C_6^{(g)}$, we find

$$U_g(R) = -\frac{C_6^{(g)}}{R^6} + \Delta(R), \quad \text{with } \Delta(R) \equiv \frac{\hbar|\Omega|^2}{4\delta(R)}, \quad (6)$$

where $\hbar\delta(R) = \hbar\delta + \Delta C_6^{(r)}/R^6$, with $\Delta C_6^{(r)} = C_6^{(r)} - C_6^{(g)}$. In the large R -limit such that $\Delta C_6^{(r)}/R^6 \ll \hbar|\delta|$, the long-range behavior of $U_g(R)$ is given by

$$U_g(R) \rightarrow -\frac{C_6^{(g)} + |b|^2 \Delta C_6^{(r)}}{R^6} + |b|^2 \hbar\delta = -\frac{C_6}{R^6} + |b|^2 \hbar\delta, \quad (7)$$

where $b = \Omega/(2\delta)$ is the mixing parameter defined before. In Eq. (7), the first term is a change of the effective C_6 due to Rydberg-dressing, which agrees with the result discussed before, and the second term represents a shift of the collision threshold (absent in our previous discussion). At shorter distance where $\Delta C_6^{(r)}/R^6 \gg \hbar|\delta|$, the term $\Delta(R)$ becomes negligible compared to $C_6^{(g)}/R^6$ in Eq. (6) as it smoothly goes to zero; only the long-range part of the interaction is modified by the blue-detuned Rydberg-dressing field. The transition between the two regimes is shown in Fig. 2(c).

Similarly, the curve between the Rydberg atom and the molecule is dressed by the laser, effectively shifted down by $\Delta(R)$: (with $|\Omega/\delta| \ll 1$ and $C_6^{(r)} > C_6^{(g)}$)

$$U_r(R) = -\frac{C_6^{(r)}}{R^6} - \hbar\delta - \Delta(R), \quad (8)$$

which, in the large R -limit ($\Delta C_6^{(r)}/R^6 \ll \hbar|\delta|$), becomes

$$U_r(R) \rightarrow -\frac{C_6^{(r)} - |b|^2 \Delta C_6^{(r)}}{R^6} - (1 + |b|^2) \hbar\delta. \quad (9)$$

This implies a slightly smaller effective van der Waals coefficient and slightly larger effective detuning.

To compute the effect of Rydberg-dressing on chemical reactions, we adopted the H_2+D electronic ground PES of Ref. [41], already tested at ultracold temperatures [39]. The potential $V(\mathbf{r}) \equiv V(r_{12}, r_{23}, r_{13})$ depends on the internuclear distances $\mathbf{r} \equiv \{r_{12}, r_{23}, r_{13}\}$, where 1 stands for D , and 2 and 3 for the two identical H atoms. The distances between H_2 and D then is simply given as $R = \frac{1}{2}\sqrt{2(r_{12}^2 + r_{31}^2) - r_{23}^2}$. Similar to Eq. (6), the three-body surface of H_2 interacting with a blue-detuned Rydberg-dressed D atom can be written as

$$\tilde{V}(\mathbf{r}) = V(\mathbf{r}) + \Delta(R), \quad (10)$$

where the blue-detuning ensure the smooth transition from the dressed long-range PES to the bare PES at shorter R without incurring possible avoided-crossing for red-detunings [45]. We choose b so that the transition occurs far enough from the van der Waals complex well (minimum of the blue curve in Fig. 2). We obtain the S -matrix by performing a fully quantum mechanic scattering calculation using the ABC code of Manolopoulos and coworkers [46] modified for the ultracold regime [39, 47]. The state-to-state cross sections are given by

$$\sigma_{q' \leftarrow q}^J(E) = \frac{\pi}{k_q^2 (2j+1)} \sum_{\ell, \ell'} |\delta_{q'q} - S_{q'\ell'q\ell}^J(E)|^2, \quad (11)$$

where $q = \{a, v, j\}$ is the set quantum numbers describing the molecular state (vibration v , rotation j , and arrangement a): a distinguishes the final state H_2+D (quenching) from $HD+H$ (reaction). J is the three-body total angular quantum number, and ℓ indicates the relative angular momentum between the initial reactants H_2 and D . The scattering wave number k_q is defined by

$$\hbar^2 k_q^2 \equiv E_c = 2\mu_{H_2+D} [E - (\varepsilon_{v,j} + |b|^2 \hbar\delta)], \quad (12)$$

where E_c is the collisional energy and $\varepsilon_{v,j}$ is the initial rovibrational energy of H_2 (in state $\{v, j\}$), $|b|^2 \hbar\delta$ corresponds to the shift due to the Rydberg dressing shown in Eq. (7), and $\mu_{H_2+D}^{-1} = m_{H_2}^{-1} + m_D^{-1}$ is the reduced mass. We define the total energy-dependent inelastic rate as

$$\kappa_{\text{in}}(E) = v_{\text{rel}} \sum_{J, q' \neq q} (2J+1) \sigma_{q' \leftarrow q}^J(E), \quad (13)$$

where $v_{\text{rel}} = \hbar k_q / \mu_{H_2+D}$ is the relative velocity. The sum is over all final channels but the entrance channel. Quenching/reaction rates ($\kappa_{Q/R}$) are obtained by splitting the sum with $a' = a$ and $a' \neq a$, respectively [39].

Numerical results for κ_{in} in the “bare” case ($|b| = 0$) for $H_2(v = 0, 1, 2, j = 0) + D$ are shown in Fig. 3(a). Resonances occur for both $v = 0$ and 1, but not 2; the s -wave ($\ell = 0$) and p -wave ($\ell = 1$) components are also shown, revealing the p -wave nature of these resonances. By varying the amount of Rydberg-dressing $|b|$, the resonances can be moved substantially, while the non-resonant $v = 2$ is only slightly affected. In these calculations, we fix

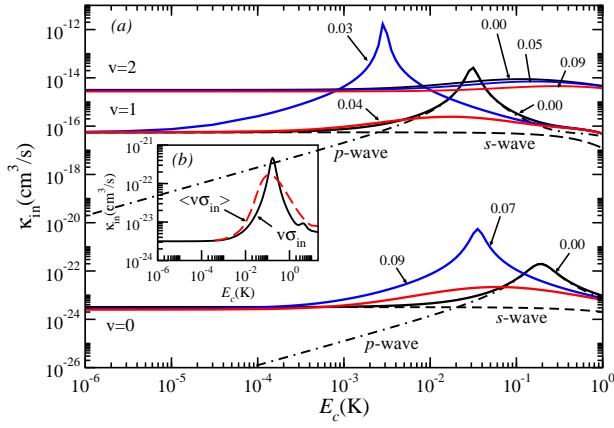


FIG. 3: (Color online) (a) κ_{in} vs. E_c for different Rydberg mixing $|b|$ (given for each curve), for $\text{H}_2(v=0, 1, 2, j=0)+\text{D}$. For the bare case ($|b|=0$) of $v=0$ and 1, the s -wave (dashed line) and p -wave (dot-dashed line) components are shown. (b) Comparison of κ_{in} and its thermal average.

$\delta \approx 296.09 \times 2\pi$ GHz, so that the threshold shift $|b|^2 \hbar \delta$ of U_g affects the position of the bound state in the entrance arrangement of the van der Waals complex. Even a modest $|b|$ is sufficient to move a resonance significantly (cases $v=0$ and 1), while much larger values are required if the van der Waals complex is not just about to support a new bound-state ($v=2$). Thus we limit our investigation to values of $|b| = |\Omega/(2\delta)| \leq 0.1$, implying a laser intensity less than $3 \times 10^8 \text{ W/cm}^2$. The $v=1$ level is particularly sensitive to a weak amount of Rydberg-dressing, with the resonance having a larger magnitude and moving to much lower energy for $|b|=0.03$, and simply disappearing for a slightly larger $|b| \approx 0.04$, when the quasi-bound state in the van der Waals complex becomes bound. Figure 3(b) compares the bare κ_{in} ($v=0$) with its thermal average (using a Maxwell distribution of v_{rel} characterized by a temperature T): the agreement between both will become better as the resonance moves to lower E_c .

Figure 4 shows this sensitivity of κ_{in} ($v=1$) by vary-

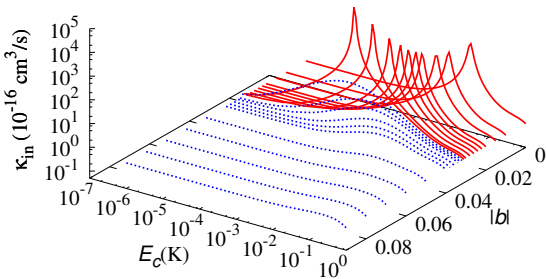


FIG. 4: (Color online) κ_{in} of $\text{D}+\text{H}_2(v=1, j=0)$ as a function of $|b|$ and E_c . The solid red curves show the inelastic rate with resonances when the $\text{H}_2 \cdots \text{D}$ complex is not yet bound, and the dashed blue curves show the case when the complex becomes bound. Both E_c and κ_{in} are on a logarithmic scale.

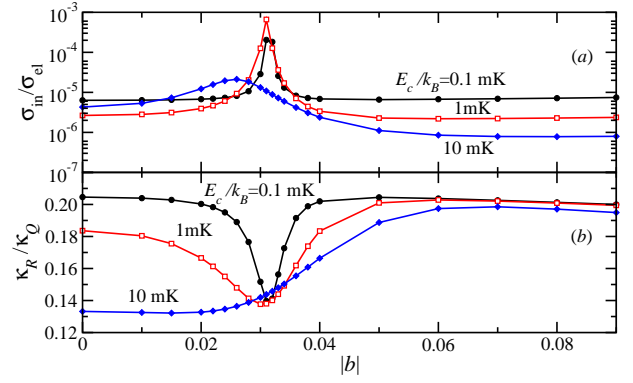


FIG. 5: (Color online) Ratios between inelastic and elastic cross sections (a), and between reaction and total inelastic rates (b), for three energies as a function of $|b|$.

ing $|b|$ and E_c ; as $|b|$ increases, the resonance shifts to lower E_c with an increased magnitude until it disappears near $|b| \approx 0.04$, at which point the van der Waals complex acquires a new bound-state. As $|b|$ increases still, the maximum in κ_{in} starts shifting to larger E_c with a decreasing magnitude. This example shows that one can, with modest Rydberg-dressing, adjust and control κ_{in} in chemically active systems, by not only moving the position of resonances but also increasing their magnitude by several orders. For example, if E_c (or temperature) of a given experiment is near the resonance, the rate could be reduced by moving the resonance away, or in cases where E_c is not near the resonance, Rydberg-dressing could move it to the right energy range. The ratio of inelastic to elastic cross sections in Fig. 5(a) shows the sharp increase (near $|b| \approx 0.03$) in relative inelasticity. Note that elastic processes are less relevant from a chemical perspective since reactants stay in their initial states. The branching ratio $\kappa_R/\kappa_{\text{in}}$ for $v=1$ in Fig. 5(b) shows how chemical reactions can be controlled within a factor of two by varying $|b|$ near 0.03; for $v=0$, where only reaction channels exist [39], the reaction rate can be changed by several orders of magnitudes (see Fig. 3). Fig. (5) suggests that the ratios $\sigma_{\text{in}}/\sigma_{\text{el}}$ and $\kappa_R/\kappa_{\text{in}}$ can be modified and controlled by Rydberg dressing.

In conclusion, we have shown that ultracold chemical reactions can be manipulated and modified using Rydberg-dressing. Although the concept was illustrated by dressing an atom approaching a diatomic molecule using the benchmark H_2+D system, this approach is general and could be applied to a wide range of systems. If the molecule has a permanent dipole moment, *e.g.* for the system $\text{LiH}+\text{H}$, Rydberg-dressing the atom would lead to a long-range interaction dominated by strong dipole induced C_6 due to the large dipole of LiH . With additional external electric fields, strong dipole-dipole interaction will become important. These strong long-range interaction might eventually lead to different branch ratios into exit channels. We note that Rydberg-dressing the final

products instead of the reactants might allow one to direct the flux of probability into specific channels, and thus to control the branching ratios for different final channels. This would open up the possibility of state-to-state control of chemical reactions.

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